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NANOMATERIALS FOR CONCRETE TECHNOLOGY

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ABSTRACT

In this paper we have discussed the current research work regarding application of nanotechnology in cement-based materials is either related to coating or enhancement of mechanical properties. It has been observed that the inclusion of nano particles would improve the toughness, shear, tensile and flexural strength of cement based materials. Some of the widely reported nanoparticles in cement concrete industries s are based on Titaniumdioxide (TiO2), Nanosilica (SiO2), Alumina (Al2O3), ZrO2, Carbon nanotube (CNT) nanoclay, etc. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles. In this paper we also discussed the general experimental methods like compressive stress, split tensile strength and Flexural strength that are carried out in order to determine strength of nanocement. Further, we have discussed the latest reliable properties like waterproofing, acid resistive and self healing qualities of nanocement. This paper will be very much useful those would like to work in the field of nanocement technology.

KEYWORDS: Nanotechnology, Nano Powder, Nanoclay, Nanoconcrete, Nanocement

INTRODUCTION

Today nanotechnology has advanced applications in the field of construction and building materials [1]. But nanotechnology in concrete on a commercial scale application remains limited with few results successfully converted into marketable products. The main progress has been done in the nanoscience of cementitious materials [2,3] with an increase in the knowledge and understanding of basic phenomena in cement at the nanoscale (e.g., structure and mechanical properties of the main hydrate phases, origins of cement cohesion, cement hydration, interfaces in concrete, and mechanisms of degradation). Recent strides in instrumentation for observation and measurement at the nanoscale are providing a wealth of new and unprecedented information about concrete, some of which is confounding previous conventional thinking. The nanoscience and nano-engineering, sometimes called nano modification, of concrete are terms that have come into common usage and describe two main avenues of application of nanotechnology in concrete research [2, 3]. Nanoscience deals with the measurement and characterization of the nano and micro scale structure of cement-based materials to better understand how this structure affects macro scale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. Nano-engineering encompasses the techniques of manipulation of the structure at the nanometer scale to develop multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: self-sensing capabilities, self-cleaning, self healing, high ductility, and self-control of cracks. Even though a huge and alluring potential of nanotechnology in civil engineering has been envisaged and enormous efforts throughout the world are being taken up to use nanotechnology in civil engineering applications, still few of grey areas need to be explored to make the technology more applicable[2-7].

Due to this, the present paper reviews the main developments in the field of nanotechnology and nanoscience research in concrete, along with their implications and key findings. Further, the interest in nanotechnology concept for portland cement composites is steadily growing. So, in this paper we discuss the most reported research work regarding application of nanotechnology in cement-based materials is either related to coating or enhancement of mechanical and electrical properties. Some of the widely reported nanoparticles in cement concrete industries are Titaniumdioxide (TiO2), Nanosilica (SiO2), Alumina (Al2O3), ZrO2, Carbon nanotube (CNT) nanoclay, etc. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles [8-9]. In this paper we also discuss on general experimental methods like compressive stress, split tensile strength and Flexural strength that are carried out to determine strength of nanocement. Further, we have discussed about waterproofing, acid resistive and self healing qualities of nanocement.

NANO CONCRETE AND NANO INGREDIENTS

Nanoconcrete made with portland cement in which particle sizes ranging from a few nanometer to a maximum of about 100 micrometers and in Nano ingredients with at least one dimension of nano meter size. The various constituents of nanocement are as shown in Figure1 [10]. So the particle size has to be reduced in order to obtain nano-portland cement. Further, if these nano-cement particles are processed with nanotubes and reactive nano-size silica particles, then strong, tough, more flexible, cement can be developed with enhanced properties.

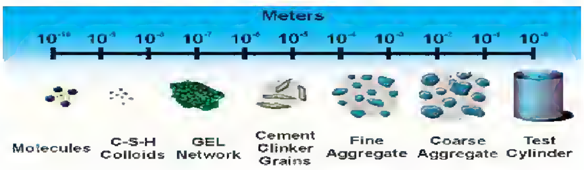

Figure 1: Scales of Various Constituents of Concrete [10]

The Nano-Filler particles are particles smaller than (0.09mm) and they can be prepared by simple methods, like sedimentation or washing method. Figure 2 demonstrates the usage of various sizes of materials available in concrete construction [11].

Nanosilicon Di Oxide

Current research activity in concrete using nano cement and nano silica includes: (i) Characterization of cement hydration (ii) Influence of the addition of nano-size silica to concrete (iii) Synthesis of cement using nano particles and coatings (applied to protect concrete).

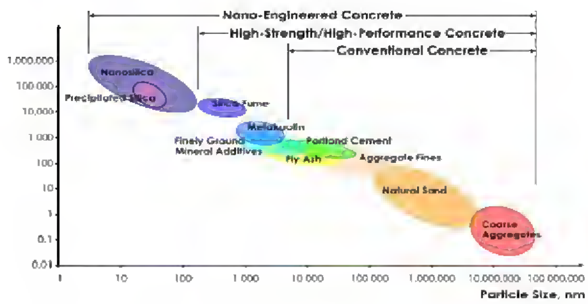

Figure 2: Various Sizes of Materials Used in Concrete [11]

In order to utilize these unique advantages, many researchers have attempted to improve the behaviour of cementitious matrix by incorporating nano silica. Especially the Nano silica in concrete or mortar will increase the density, reduces porosity, and improves the bond between cement matrix and aggregates [12]-[15] with higher compressive and flexural strength [16]. The compressive strength evaluation of cement mortar with nS and with silica fume was discussed for different w/c ratio [17]-[18]. From the experimental results it is confirmed that the compressive strength of mortars with nS were higher than those of mortars containing silica fume at 7 and 28 days. Figure 3 shows how the mineral additive takes in the cement constituent and nano-SiO2 [11]. It was proved from the earlier studies by Qing et.al [19] that the enhancement of strength mainly depends on nS addition rather than addition of silica fume. Also, it was found that the nS behaves not only as a filler to improve the microstructure, but also as an activator to promote pozzolanic reactions and super-plasticizer plays an important role during mixing cement with nano particles.

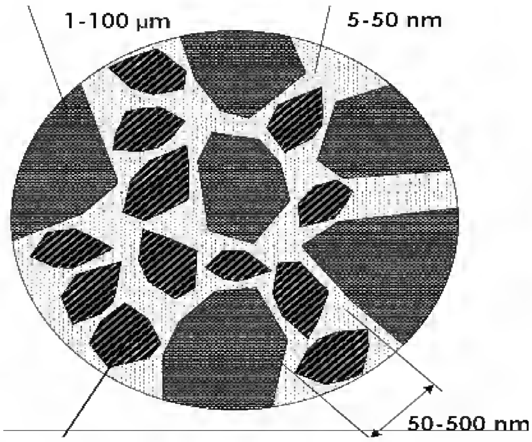

Figure 3: The Image Showing Mineral Additive, Cement Constituent and Nano-SiO2 [11]

Gaiteroa et al [20] studied and proved the effect of silica nano particles on the reduction of calcium leaching rate of cement paste and it was concluded that addition of nS can control the C-S-H degradation due to calcium leaching and can increase the overall strength of cement-based materials at every stage. Nano Silica was mostly used in making Self Compacting Concrete and High Performance Concrete. Normally those two concrete can be named as eco-concrete. The Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or other supplementary waste materials. The main problem in these types of eco-concrete is segregation. By adding nS in the corresponding mixtures and accelerates setting time and compressive strength of concrete. Nano silica is used for the preparation of rock-matching grouting, gypsum particle board, additives in tile, workability increaser, anti bleeder etc. Li et.al [21] demonstrated the effect of addition of nS in high volume fly ash concrete and the results are compared with control concrete.

Nano Titanium Di Oxide

Nazari et al [22, 23] conducted the studies on the compressive-, split tensile- and flexural, strength, and workability and setting time of concrete by partial replacement of cement with nano-phase TiO2 particles. Similar to investigations on nano SiO2 in cementious matrix, many researchers have discussed the possible methodologies and observed advantages by using nano TiO2 in cement matrix especially to achieve high compressive- and flexural- strength. Jayapalan [24] investigated the effect of chemically TiO2 nanoparticles on early-age hydration of cement and the effects of different percentage rates of added TiO2 to portland cement on early-age behavior were examined.

Nano Aluminium Di Oxide

The role of nano Al2O3 in increasing the mechanical properties of cement has been carried out by few researchers. The optimized level of usage of nano particles to attain the ultimate strength was reported. The effect of curing medium on microstructure together with physical, mechanical and thermal properties of concrete containing Al2O3 nano particles was explored by Nazari and Riahia [25]. Further, Campillo et al [26] emphasized the potential of nano materials for activation of the initial strength of belite cements. In this study two types of Al2O3 based nano materials such as an agglomerated dry alumina (ADA) with an average grain size ranging from 0.1 μm (100 nm) to 1 μm and colloidal alumina (CA) composed of 50 nm alumina nanoparticles dispersed in water was used for the activation of early strength of be lite cements. The study concluded that an addition of nano particles notably increases the early strength (7 days) and the nano particle can be used as an agent for activating hydraulic properties of belite cement thereby changes in microstructure causes improved mechanical property. The effect of nano Al2O3 on elastic modulus and compressive strength of the cement composites was brought out by Li et al [27]. The role of nano particles as a fine aggregate was confirmed through SEM and EDS study stating that the nano Al2O3 fill the ITZ of cement- sand and some capillary in the matrix and hence the elastic modulus and compressive strength of mortars were increased. But, no significant improvement in compressive strength was noticed due to insufficient filling of pores in the cement matrix under experiment condition.

Nano Zirconium Di Oxide

Nazari and Riahi [28] investigated the possibility of increasing split tensile strength of self compacting concrete (SCC) by adding ZrO2 nano particles. The results showed that inclusion of ZrO2 up to 4 wt% was able to increase the split tensile strength of SCC due to the formation of more hydrated products in presence of ZrO2 nano particles and improvement in pore structure. Further, Nazari et al [29] investigated the compressive strength and workability of concrete by partial replacement of cement with nano-phase ZrO2 particles. Further it was observed that the addition of nano-ZrO2 particles decreased the fluidity and increased the water demand for normal consistency. Therefore, the use of super-plasticizers was insisted while adding ZrO2 nano particles. A significant improvement in compressive strength was achieved. Same researchers [30] studied the split tensile- and flexural- strength together with the setting time of concrete by partial replacement of cement with nano- ZrO2 particles.

Nano Ferrous Oxide

Nazari et al [31] conducted studies on the compressive strength and workability of concrete by partial replacement of cement with nano-phase Fe2O3 particles and results were compared with control specimen. A significant achievement in high compressive strength has been obtained and also decrease in workability has been seen in presence of nano particle blended concrete. Earlier investigations suggests that inclusion of nano-phase Fe2O3 particles in cement improves the properties like split tensile- and flexural- strength together with the setting time of cement [32]. A delay in setting time was observed in nano particles blended concrete. The optimized level of usage of nano particles to attain the ultimate strength was reported. Mechanical properties such as compressive- and flexural- strengths of cement mortar containing nano particles such as nS and nano Fe2O3 (hybrid incorporation) were studied and their impressive results (improvement in both compressive and tensile strength) were reported by Li et.al [33] and the smart behaviour of nano Fe2O3 in self stress sensing was also observed which can lead to a paradigm shift in techniques for health monitoring of structures.

Carbon Nanotubes (CNTS)

Nowadays an extensive research is going on Carbon nanotubes. An addition of small amount (1% by wt) of CNT can improve the mechanical properties consisting of the main Portland cement phase and water. A CNT can be single walled or multi walled. CNTs are the strongest and most flexible molecular material with Young's modulus of over 1TPa. The approximate diameter is 1 nm with length to micron order. CNTs have excellent flexibility. These are essentially free from defects. Nanotubes are highly resistant to chemical attack and have a high strength to weight ratio (1.8g/ cm3 for MWNTs & 0.8G/cm3 for SWNTs). CNT has maximum strain of about 10% which is higher than any other material.

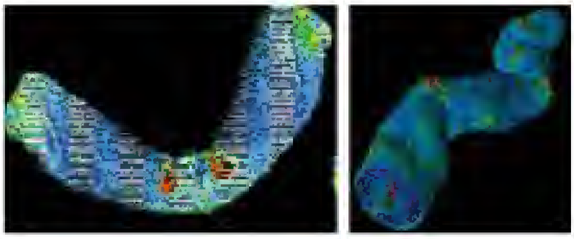

Figure 4: Flexible Behavior of CNTS

Figure 4 shows the flexible behaviour of CNTs. Due to its small particle size NMK facilitated CNTs dispersion and improved the interfacial interaction between the CNTs and the cement phases [34]. An addition of CNTs (up to 0.02%) to NMK cement mortar improves the compressive strength of the composites to great extent.

Nanoclays

Nanoclay raw material is montmorillonite; a 2-to-1 layered smectite clay mineral with a platey structure. The Naturally occurring montmorillonite is hydrophilic. Through clay surface modification, montmorillonite can be made organophilic and, therefore, compatible with conventional organic polymers. Nanoplate fillers can be natural or synthetic clays, as well as phosphates of transitionmetals. The most widely used reinforcement is clay due to its natural abundance and its very high form factor. The Clay-based nanocomposites generate an overall improvement in physical performances. The most widely used ones are the phyllosilicates (smectites). They have a shell-shaped crystalline structure with nanometric thickness. Clays are classified according to their crystalline structures and also to the quantity and position of the ions within the elementary mesh. The elementary or primitive mesh is the simplest atomic geometric pattern, which is enough for duplicating the crystalline network, by repeating itself indefinitely in the three directions. Table 1 presents the various natural and synthetic nanoclays available and used as fillers in polymers. The most common usage concerns organ modified Montmorillonite (MMT), a natural phyllosilicate extracted from Bentonite. Raw formula of Montmorilloniteis (*Na*, *Ca*) 0, 3(*Al*, *Mg*) 2Si4O10 (*OH*) 2, nH2O. [35].

Naocement Yest Methods

To test the hardness of the cement, the following simple tests have been conducted are given below[35][36], which include (a)Test for Compressive strength,(b) Test for Split tensile strength and (c) Test for Flexural strength. Based on the experimental studies presented in the paper [35], [36], it was concluded that the Compressive and tensile strength of the cement mortars with Nanoclay is higher than that of the plain cement mortar with the same w/b ratio. Further, the enhancement of compressive strength was about 300% at 1% NC nanoclay replacement and is about 290% at 2% NC for seven day testing. While for 28 day testing it was 310% for 1% NC and 200% for 2% NC. 35][36]

Figure 5: Batch of Cube Specimens Casted

Compressive Strength

Concrete cubical moulds of size 15 cm x 15cm x 15 cm are commonly used (Figure 5). The concrete is poured in the mould and tempered properly so as not to have any voids. After 24 hours these moulds are removed and test specimens are put in water for curing. The top surface of these specimens should be made even and smooth. This is done by putting cement paste and spreading smoothly on whole area of specimen. The specimens are tested by compression testing machine (Figure 6) after 7 days curing or 28 days curing. Load should be applied gradually at the rate of 140 kg/cm2 per minute till the Specimens fails. Load at the failure divided by area of specimen gives the compressive strength of concrete (Figure 7).

Figure 6: Specimen Tested for Compressive Strength

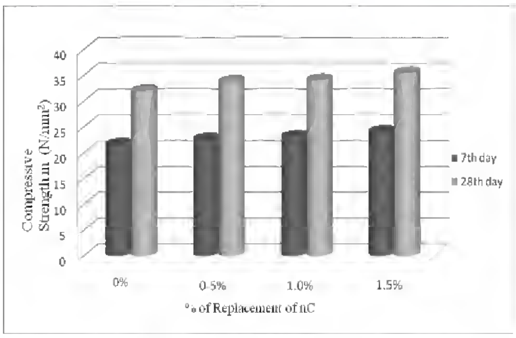

Figure 7: Compressive Strength of Concrete with and without nC (0 - 1.5 %) [36]

Split Tensile Strength

The concrete is fill in the cylinder mould in four layers each of approximately 75 mm and ram each layer more than 35 times with evenly distributed strokes. Remove the specimens from the mould after 24 hours and immerse them in

water for the final curing. The test is usually conducted at the age of 7-28 days. Apply the load without shock and increase it continuously at the rate to produce a split tensile stress of approximately 1.4 to 2.1 N/mm2/min Compute the split tensile strength of the specimen to the nearest 0.25 N/mm2 (Figure 8).

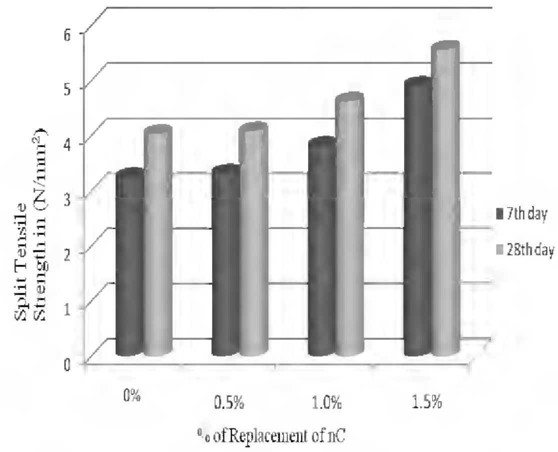

Figure 8: Split Tensile Strength of Concrete with and without nC (0 – 1.5 %) [36]

Flexural Strength

Beams shall be fabricated in sets of three (3) beams for each test age. Before each use, apply a release agent such as a light coat of fresh oil to all inside surfaces of the mold. Place the concrete in the molds, Vibrate the concrete. The duration of vibration required will depend upon the workability of the concrete and the effectiveness of the vibrator. Cover the beams with an insulating blanket to hold the heat and moisture in the beams while they cure. Apply the load continuously at a rate that constantly increases the extreme fiber stress from 0.85 MPa to 1.2 N/mm2/min, until rupture occurs (Figure 9). The average of these three Specimens is listed. [36]

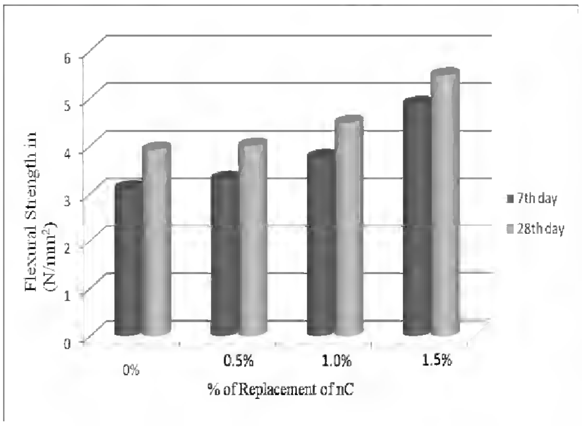

Figure 9: Flexural Strength of Concrete with and without nC (0 – 1.5 %) [36]

The nano Clay based concrete structure fill all micro holes, because it's thousand times smaller than in the case of traditional concrete materials. This allows the reduction of the cement used and gives the compression needed to reduce over 90 % of the additives used in the production of concrete. Core concrete allows saving some percentage of the used cement. The use of nano Clay help in modifying properties of concrete both in plastic and hardened stage and thus results into a more durable concrete. It has been recognized that the addition of small, closely spaced and uniformly dispersed nano Clay to concrete would act as crack arrester and would substantially improve its static and dynamic properties. Addition of nano Clay enhances the ductility performance, post-crack tensile strength, fatigue strength and impact strength

of concrete structures. The main purpose of this investigation is to study the effects of nano Clay on the workability, compressive strength, split tensile and flexural strength of M20 grade concrete. For comparison, reference specimens were tested. Experimental results show that the workability of concrete reduces with the addition of nano Clay in concrete and also the results show that the nano Clay concrete specimen's gives higher compressive, split tensile and flexural strength.

SELF HEALING PROCESS IN NANO CONCRETE

Experimentation is also underway on self-healing concrete. When self-healing concrete cracks, embedded microcapsules rupture and release a healing agent into the damaged region through capillary action. The released healing agent contacts an embedded catalyst, polymerizing to bond the crack face closed. In fracture tests, self-healed composites recovered as much as 75 percent of their original strength. They could increase the life of structural components by as much as two or three times. When cracks form in this self-healing concrete, they rupture microcapsules, releasing a healing agent which then contacts a catalyst; triggering polymerization that bonds the crack closed Figure 10. [37]

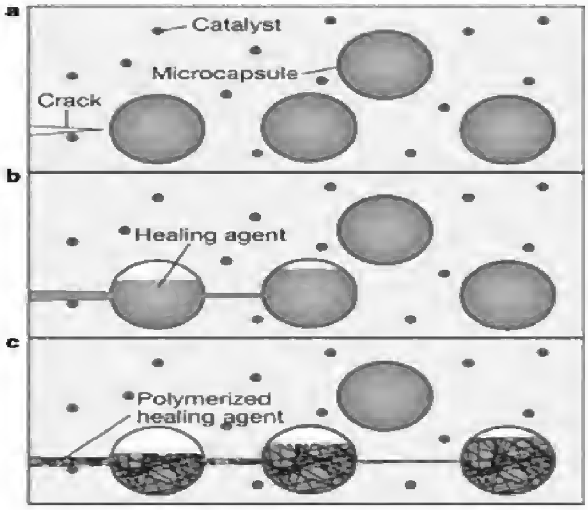

Figure 10: Mechanism of Self Healing Concrete [36]

The compressive strength results of series C0 and N mixtures are shown in Comparison of the results from the 7, 28 and 90 days samples shows that the compressive strength increases with nano-ZrO2 particles chemical up to 1.0% replacement (N2) and then it decreases, although the results of 2.0% replacement (N4) is still higher than those of the plain cement concrete (C0). It was shown that the use of 2.0% nano-ZrO2 particles decreases the compressive strength to a value which is near to the control concrete. This may be due to the fact that the quantity of nano-ZrO2 particles (pozzolan) present in the mix is higher than the amount required to combine with the liberated lime during the process of hydration thus leading to excess silica leaching out and causing a deficiency in strength as it replaces part of the cementitous material but does not contribute to strength. Also, it may be due to the defects generated in dispersion of nanoparticles that causes weak zones.

ACID RESISTANCE NANOCEMENT

The risk of acid attack on concrete can be minimized by providing due consideration to concrete porosity. Lesser the porosity, lesser will be the chances of acid attack on concrete. In general it is said that all high performance concrete mixtures show a better resistance against acid attack than the reference ordinary type concrete.[37] By High

performance concrete is meant a concrete with superior qualities including low permeability and low diffusion. In another way, the concrete resistance to acids can also be provided by giving its surface an acid resistant coating. In construction materials, the materials density and strengths are the most important properties in which the experts are interested. The High performance concrete is quite effective against acid attack. However, it is a common observation that materials having high strengths are also associated with higher densities and thus the dead weight of the structure considerably increases. [37]

CONCLUSIONS

The role and mechanism of the nano particles of various oxides with cementitious materials have been reviewed and discussed in detail. Most of the authors concluded that inclusion of nano particles will impart more uniform and compact microstructure inside the concrete. The improvement in mechanical properties such as compressive-, flexural- and split- tensile strength of concrete containing nano particles have been reviewed by several researchers. According to researchers, following is a list of areas, where the construction industry could benefit from nano-technology. (i) Replacement of steel cables by much stronger carbon nanotubes in suspension bridges and cable-stayed bridges, (ii) Use of nano-silica, to produce dense cement composite materials, (iii) Incorporation of resistive carbon nanofibers in concrete roads in snowy areas,(iv) Incorporation of nano-titania, to produce photocatalytic concrete, (v) Use of nano-calcite particles in sealants to protect the structures from aggressive elements of the surrounding environment, (vi) Use of nano-clays in concrete to enhance its plasticity and flow ability, (vii) Urban air quality could be improved by if the civil structures are treated with nano TiO_2. Although, several studies are reported, there is no clear mechanism on the Form-Structure-Function of materials as it's intended to use them in cement or concrete. Further studies based on the assessment of nano particles with respect to their high surface to volume ratio, stability and their structural elucidation when combined with other cementitious materials have to be studied in detail.

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